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TECHNICAL REPORT AR98L-TR-02143

A PRIORI ESTIMATION OF RATE CONSTANTS FOR  
UNIMOLECULAR DECOMPOSITION REACTIONS

George F. Adams

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# TABLE OF CONTENTS

	Page
I. INTRODUCTION. . . . .	5
II. REVIEW OF THEORY. . . . .	6
III. A PREDICTED RATE CONSTANT FOR METHOXY RADICAL DECOMPOSITION. . . . .	9
IV. A PREDICTED RATE CONSTANT FOR FORMYL RADICAL DECOMPOSITION. . . . .	19
V. SUMMARY . . . . .	25
REFERENCES. . . . .	27
DISTRIBUTION LIST . . . . .	29

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## I. INTRODUCTION

There are a hierarchy of models that describe the phenomenology of double-base propellants. Interior ballistics codes accept propellant data as inputs, and predict pressure vs. time curves, muzzle velocities, etc. Consideration of these models is beyond the scope of this research, and the mention is made only to set limits to the capabilities of other models.

Among other inputs, propellant combustion modelers try to predict the regression rate of a burning propellant. A model to predict the regression rate of a solid requires knowledge of many properties, such as,

- (1) Solid-state reactivity and heat release,
- (2) Gas-phase chemistry,
- (3) Gas-phase transport properties,
- (4) Coupling mechanism between the gas and condensed phases.

Little information is available for any of these properties, although recent work in this laboratory may shed light on items two and three<sup>1,2</sup>. In particular, Kooker's modeling provides the first realistic coupling of chemistry and hydrodynamics for a confined reacting gas mixture.

The research described in this report was motivated by the need for pressure and temperature dependent rate-constant expressions for the unimolecular decomposition reactions of two free-radical species, methoxy radical ( $\text{CH}_3\text{O}$ ) and formyl radical ( $\text{HCO}$ ). Such data are required for qualitative kinetic modeling of the primary flames of simple, mono-nitrate esters. Models of the primary flames for this class of compounds should provide transferable data for models of the gas-phase reactions for burning propellants.

Pressure and temperature dependent rate constants for unimolecular reactions can be predicted by application of the Rice-Ramsperger-Kassel-Marcus (RRKM) theory. The next section reviews the major features of this theory, and subsequent sections deal with the application of the method to methoxy radical and formyl radical.

1. R.A. Fifer, "High Temperature Pyrolysis of Methyl and Ethyl Nitrate", Seventeenth Combustion Institute Symposium preprint.
2. D.A. Kooker, "Transient Laminar Flame Propagation in Confined Premixed Gases; Numerical Prediction.", Seventeenth Combustion Institute Symposium, preprint.

## II. REVIEW OF THEORY

A recent report reviews the development and application of RRKM<sup>3</sup>. More complete discussions of the theory for unimolecular reactions can be found in texts by Forst<sup>4</sup> and Robinson and Holbrook<sup>5</sup>. Several points about the theory require that a modest overview precede discussing the results of this project.

The Lindeman theory forms the basis of almost all modern treatment of unimolecular reactions. The mechanism consists of three steps:

- (1) An energizing collision between the reactant, A, and a collision partner, M, produces an energized molecule A\*.



The energized molecule possesses energy greater than a critical energy,  $E_0$ . The critical energy is the minimum energy the species A must possess in order to undergo a chemical transformation.

- (2) Energized molecules are de-energized by collision.



The Lindeman theory assumes that every collision of A\* leads to de-energizing.

- (3) A time-lag exists between the energizing of A and the unimolecular reaction of the energized molecule.



The chemical rate coefficients are assumed to be constants. By application of the steady-state hypothesis to the concentration of A\*, an equation for the overall rate of reaction can be written,

$$v = k_3(A^*) = k_1 k_3(A)(M) / (k_2(M) + k_3) \quad (4)$$

3. G.F. Adams, "An Analysis of the Pressure Dependence of Nitrate Ester Thermal Decomposition", ARBRL-TR-02106. (AD #A063513)
4. W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, 1973.
5. P.J. Robinson and K.A. Holbrook, "Unimolecular Reactions", Wiley Interscience, New York, 1972.



There are two important limiting cases. At high pressures,  $k_2(M) \gg k_3$ , so that

$$v_{\infty} = \frac{k_1 k_3}{k_2} (A) = k_{\infty} (A). \quad (5)$$

At low pressures,  $k_3 \gg k_2 (M)$ , and

$$v_{bim} = k_1 (A) (M), \quad (6)$$

a rate that depends on the second-order energy-transfer rate constant.

Lindeman's theory predicts that the unimolecular rate coefficient is not constant for low concentrations, but is constant at high-pressures. These predictions are qualitatively correct, but quantitative predictions based on this theory are never correct, principally because the rate coefficients  $k_1$ ,  $k_2$ ,  $k_3$  are not constants. Modifications to Lindeman's theory led to development of the RRKM theory. The predictions of RRKM theory agree with experiment. A review of the application of the RRKM method has been given<sup>3</sup>. The emphasis here is that the reactions proceed with variable molecularity - bimolecular at low pressure, unimolecular at high pressure, and, in the transition region between these two limits, with a variable molecularity. Figure 1 illustrates the various regions, showing a plot of the unimolecular rate coefficient,  $k_{uni}$ , versus P for a hypothetical reaction. It is the purpose of this report to describe the pressure-dependence of the decomposition reactions for the methoxy and formyl radicals, and to provide, in the case of methoxy, a pressure-dependent rate expression for the transition region.

The following sections describe the methoxy radical decomposition and the formyl radical decomposition. To predict the rate constants for these reactions, it is necessary to have information concerning the molecular properties of the reacting system. Specifically, one needs to know:

1. The critical energy,  $E_0$ , for the decomposition reaction,
2. The vibrational frequencies for the reactant molecule and the energized molecule,
3. The molecular structure parameters, bond lengths and angles, for the reactant molecule and the energized molecule.

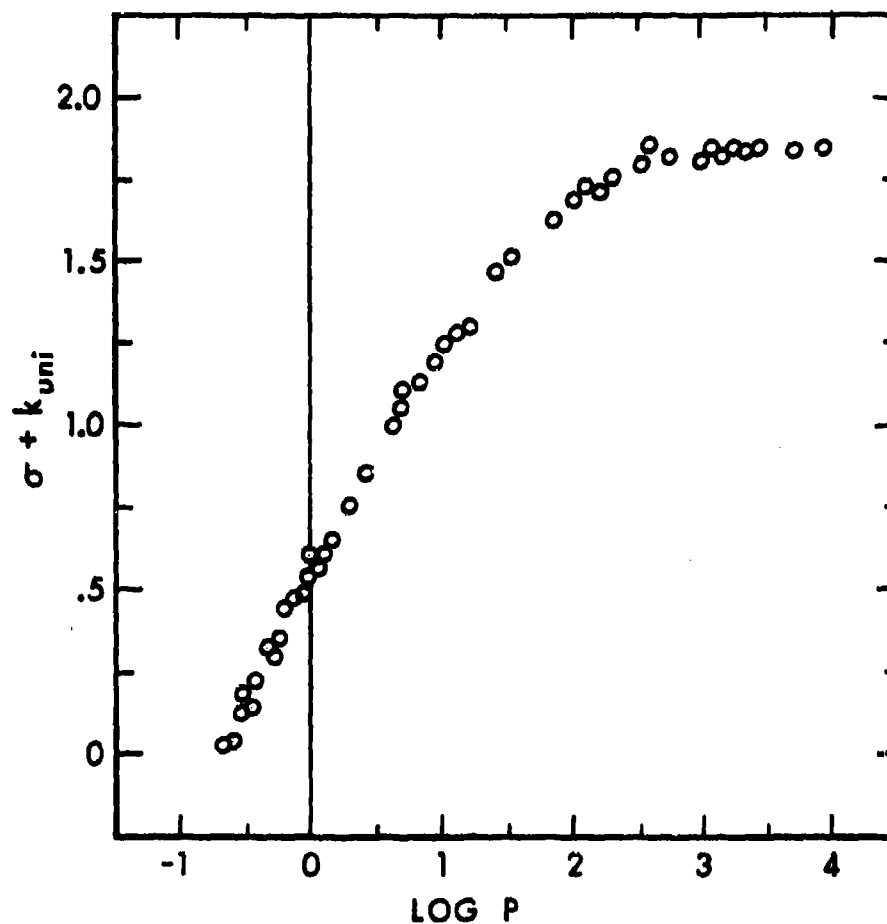


Figure 1. Variation of  $k_{uni}$  with pressure. At low pressure the rate coefficient is a linear function of pressure, while at high pressure the rate coefficient is constant.



### III. A PREDICTED RATE CONSTANT FOR METHOXY RADICAL DECOMPOSITION

The methoxy radical,  $\text{CH}_3\text{O}$ , is a rara avis. Attempted spectroscopic studies of the molecule have produced a spectral signature, but not enough data to provide a molecular structure for the compound<sup>6</sup>. A theoretical quantum chemical study of the electronic structure of the radical has provided an estimate of the bond lengths and angles<sup>7</sup>. Yarkony, et al., found that the bond lengths for  $\text{CH}_3\text{O}$  were approximately equal to the respective bond lengths in methanol. Further, the theoretical results imply that the C-O bond is not perpendicular to the plane of the three hydrogens, but is bent three degrees toward the two equivalent hydrogens. This staggered arrangement breaks the  $\text{C}_3$  symmetry of the methyl group, leaving only a plane of symmetry. The predicted structure provides the data needed to compute the moments of inertia for the reactant. In addition, since the predicted structure is so close to that of methanol, the vibrational frequencies for the reactant are assumed equal to those for methanol. These estimates and the computed moments are presented in Table 1.

Because the theoretical study of methoxy included no details of the potential energy hypersurface, no structure was predicted for the transition state. Decomposing methoxy to form formaldehyde and a hydrogen atom requires several structural changes:

1. The stretching of a C-H bond to an effectively infinite length,
2. The flattening of the methyl group, leaving a planar  $\text{CH}_2$  terminus,
3. The shortening of the C-O bond.

None of these changes will be complete at the transition state, however. The model used here is obtained by making the following assumptions.

6. H.E. Radford and D.K. Russell, "Spectroscopic Detection of Methoxy ( $\text{CH}_3\text{O}$ )", J. Chem. Phys. 66, 2222 (1977).
7. D.R. Yarkony, H.F. Schaeffer, III and S. Rothenberg, "Geometries of the Methoxy Radical ( $X^2E$  and  $A^2A_1$  States) and the Methoxide Ion", J. Am. Chem. Soc., 96, 656 (1974).

1. The "in-plane" C-H bond is stretched to a bond length of 3.5 Å.
2. The CO bond length is shortened to 1.3 Å, between the values for methoxy and formaldehyde.
3. The O-CH<sub>2</sub> bond angle is reduced by approximately ten degrees.

Table 1. Molecular Data for Methoxy Radical and Excited Complex<sup>a</sup>.

Property	Radical	Complex
R <sub>CH</sub>	1.08	3.5
R <sub>CO</sub>	1.44	1.3
θ <sub>OCH</sub>	109°	109°
E <sub>O</sub>	24 kcal mol <sup>-1</sup>	
I <sub>xx</sub>	19.5	25.3
I <sub>yy</sub>	19.53	17.1
I <sub>zz</sub>	3.62	11.3
ν <sub>1</sub>	2977	2980
ν <sub>2</sub>	2977	2840
ν <sub>3</sub>	2844	0000
ν <sub>4</sub>	1477	1400
ν <sub>5</sub>	1455	1000
ν <sub>6</sub>	1430	300
ν <sub>7</sub>	1171	300
ν <sub>8</sub>	1112	850
ν <sub>9</sub>	1029	850

<sup>a</sup>Bond distances are given in Å, moments of inertia in amu-Å<sup>2</sup>, and vibrational frequencies in wave numbers.

Stretching of the CH bond causes one of the C-H stretching frequencies to approach zero, and reduces four of the six methyl bending modes. Estimates of the vibrational frequencies for the energized molecule and the computed moments of inertia are given in Table 1.

The vibrational frequencies and moments-of-inertia assumed for the methoxy radical and the transition species are used to compute the rotational and vibrational partition functions. In addition, a value for the high-pressure Arrhenius factor can be estimated.

To perform the RRKM integration, these factors must be supplemented by a value for the energy barrier to the unimolecular reaction. Figure 2 shows a schematic plot of potential energy versus an arbitrary reaction coordinate. The potential energy barrier, indicated by  $E$ , is the simple difference in the electronic energy for the two configurations. This number must be corrected to include the difference in the zero point vibrational energies for the two structures, giving a value for the critical energy,  $E_0$ . Integration of the RRKM equation for the unimolecular rate constant requires a knowledge of the critical energy. Since no experimental value for this parameter is available, an estimate must be made.

Among thermochemical data available for methoxy is the dissociation energy relative to formaldehyde<sup>8</sup>,  $D(\text{H}-\text{CH}_2\text{O}) \approx 29 \text{ kcal mol}^{-1}$ . It is common to find empirical estimates of activation energies that are lower than the dissociation energy, often by five  $\text{kcal mol}^{-1}$ , or more. Applying this empirical rule, a value of  $24 \text{ kcal mol}^{-1}$  is assigned to the activation energy,  $E_a$ , which is assumed to equal the critical energy. A thermochemical argument by Batt and McCulloch estimates  $E_a = 25 \text{ kcal mol}^{-1}$ . The uncertainty associated with the two methods of estimation suggest that this near agreement is fortuitous. Predictions of  $k_{\text{uni}}$  for the methoxy radical decomposition are made by assuming  $E_0 = 24 \text{ kcal mol}^{-1}$ . An alternative theoretical method for estimating  $E_0$  is presented in the discussion of the results for the formyl radical decomposition.

To complete describing the analytical method used to predict the rate constant, it is noted that the sums and densities of quantum states were calculated via the Whitten-Rabinovitch semiclassical method<sup>9</sup>. A discussion of the application of the method is given in references (3) and (5).

8. J. Heicklen, "Gas Phase Reactions of Alkylperoxy and Alkoxy Radicals", Adv. Chem. Ser., No. 76, 23 (1974).
9. G.Z. Whitten and B.S. Rabinovitch, "Accurate and Facile Approximation for Vibrational Energy-Level Sums", J. Chem. Phys., 38, 2466 (1963).

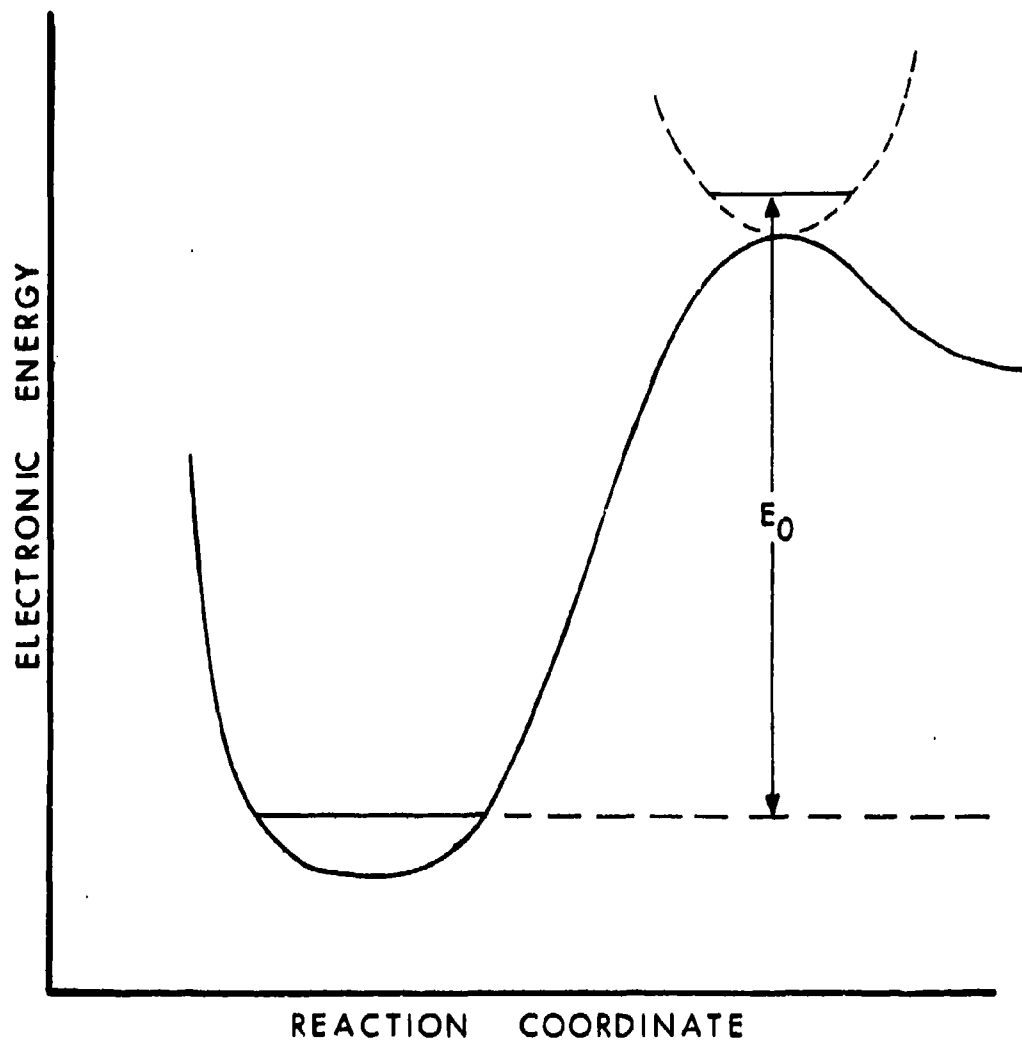


Figure 2. A schematic representation of the variation of electronic energy with reaction progress. The critical energy is shown as the difference between the lowest total energy state of the reactant and the transition state.

The rate-constant for the methoxy radical decomposition was computed at four temperatures: 900°, 1000°, 1100°, and 1200°K. The results of the four calculations are shown in Table 2. The kinetics data is summarized in Figure 3, where the hatched area identifies the pressure range of interest for the pyrolysis model. This area obviously lies in the fall-off portion of the rate-constant curves; thus neither the high-pressure nor the low-pressure limit for the rate expression will be valid for the modeling.

The pressure dependence of the unimolecular rate constant demonstrates the competition between the collisional energy transfer and intramolecular relaxation. These two processes, essentially decoupled in the low- and high-pressure limits, overlap in the intermediate part of the "fall-off" region. Troe has suggested that the difficult analysis of the intermediate fall-off curve should be based on information derived from the two limiting rate constants<sup>10</sup>. Troe derived a general first-order rate constant  $k/k_\infty$  as a measure of pressure. His analysis concluded that the reduced fall-off curves do not depend strongly on the theoretical model of the reaction. This suggests that even simple theoretical models are sufficient to predict reduced fall-off curves useful for extrapolating experimental data.

Troe's objective was to predict the entire fall-off region well enough to extrapolate data from one limiting case to another. The goal of the present research is to derive a rate constant expression that adequately describes a relatively small part of the rate constant curve. Following Troe, a reduced rate constant  $k/k_\infty$  is defined.

Assuming that  $k_\infty$  can be expressed by an Arrhenius-expression

$$k_\infty = A_\infty e^{-E_0/RT}, \quad (7)$$

there are two alternatives for defining  $A_\infty$ :

1. Let  $A_\infty = A_\infty(T)$  for the temperature of interest.
2. Define a single, average high-pressure frequency factor  $\bar{A}_\infty = \langle A_\infty(T) \rangle_T$ .

10. J. Troe, "Fall-Off Curves of Unimolecular Reactions", Ber. Bunsenges. physik. Chem., 78, 474 (1974).

Table 2. Predicted  $k_{uni}$  for Methoxy Radical<sup>a</sup>.

Pressure (torr)/Temperature (°K)	900	1000	1100	1200
10	4.5(5)	1.5(6)	3.9(6)	8.3(6)
100	4.4(6)	1.5(7)	3.8(7)	8.2(7)
760	2.9(7)	9.9(7)	2.7(8)	5.9(8)
1000	3.6(7)	1.3(8)	3.4(8)	7.6(8)
1520	5.1(7)	1.8(8)	4.9(8)	1.1(9)
3800	9.6(7)	3.5(8)	1.0(9)	2.4(9)
5000	1.1(8)	4.2(8)	1.2(9)	2.9(9)
7600	1.4(8)	5.4(8)	1.6(9)	3.9(9)
10000	1.6(8)	6.3(8)	1.9(9)	4.7(9)
11400	1.7(8)	6.7(8)	2.1(9)	5.1(9)
15200	1.9(8)	7.7(8)	2.4(9)	6.0(9)
20000	2.1(8)	8.6(8)	7.8(9)	7.0(9)
30000	2.4(8)	1.0(9)	3.3(9)	8.5(9)
38000	2.6(8)	1.1(9)	3.6(9)	9.4(9)
50000	2.7(8)	1.2(9)	4.0(9)	1.0(10)
76000	3.0(8)	1.3(9)	4.5(9)	1.2(10)
100000	3.1(8)	1.4(9)	4.9(9)	1.3(10)
114000	3.2(8)	1.4(9)	5.0(9)	1.4(10)
150000	3.3(8)	1.5(9)	5.3(9)	1.5(10)
200000	3.4(8)	1.5(9)	5.6(9)	1.6(10)
$Q_1$	14875	16122	18600	21194
$Q_1^\ddagger$	28012	32808	37850	43128
$Q_2$	2.466	3.09	3.9	4.95
$\log A_\infty$	15.39	15.5	15.56	15.61

<sup>a</sup> Notation: 4.1(5) implies  $4.1 \times 10^5$ . Statistical mechanical parameters are dimensionless.

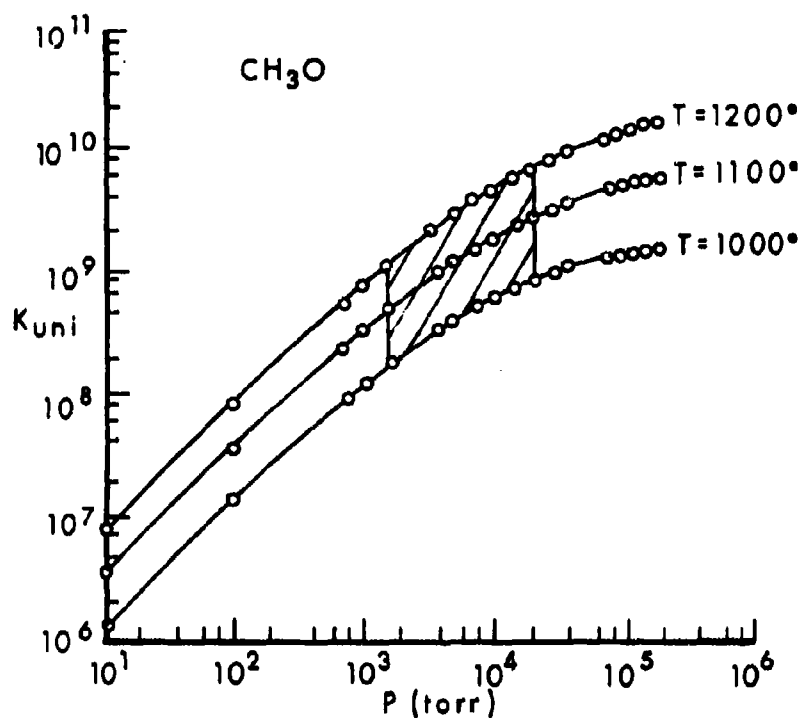


Figure 3. Variation of  $k_{\text{uni}}$  with pressure for the decomposition of methoxy at three temperatures, 1000°K, 1100°K and 1200°K. The hatched area identifies the physical conditions encountered in Fifer's experiments (1).



The energy in the Arrhenius expression, Equation 7, is assumed to be the critical energy,  $E_0$ . Table 3 contains the results of computing  $k/k_\infty$  for each choice of  $A_\infty$ , at various pressures and temperatures corresponding to those encountered in the pyrolysis experiments. Figure 4 presents a plot of  $\log(k/k_\infty)$  versus  $\log P$  for the case  $A_\infty = \langle A_\infty(T) \rangle$ . The plot shows that, to reasonable accuracy, a single line could be used to describe these data. Table 4 lists the average  $k/k_\infty$  ratios for pressures in the range,  $2 \text{ atm} \leq P \leq 20 \text{ atm}$ . A plot of  $\log(k/k_\infty)$  versus  $\log(P)$ , using the average values for the reduced rate constant has a slope,  $m$ , of 0.65. To derive the final expression for the unimolecular rate constant, the following equation must be integrated.

$$d \log \frac{k}{k_\infty} = m \quad d \log P. \quad (8)$$

The integration has a lower-limit at  $P_1 = 1520 \text{ torr}$ , where  $(k/k_\infty)_1 = .0095$ . The integrated expression is

$$\log(k/k_\infty) - \log(k/k_\infty)_1 = m(\log P - \log P_1). \quad (9)$$

Rearranging,

$$k/k_\infty = (k/k_\infty)_1 (P/P_1)^m \quad (10)$$

$$= .0095 (P/1520)^{0.65}, \quad (11)$$

so that

$$k = k_\infty (.0095) (P/1520)^{0.65}, \quad (12)$$

$$\text{where } k_\infty = 3.31 \times 10^{15} \exp(-24000/RT). \quad (13)$$

Kineticists often prefer that the rate-constant expression replace the pressure variable with a density variable. Performing this manipulation yields the following expressions for the rate constant,

$$k = k_\infty (.0095) \left( \frac{\rho T}{.0244} \right)^{0.65} \quad (14)$$

In order to evaluate the validity of the derived rate-constant expression, values of  $k_{\text{uni}}$  predicted using this expression are compared with the results of the original RRKM integration. The data presented in Table 5 show that the derived rate-constant expression is an excellent approximation for describing the unimolecular decomposition rate for

Table 3. ( $k_{uni}/k_{\infty}$ ) for Two Choices of  $A_{\infty}$ .

I. Pre-exponential factors taken from Table 2.

Temperature	900	1000	1100	1200
Pressure (torr)				
1520	.013	.01	.0081	.0064
3800	.025	.02	.017	.014
5000	.03	.024	.02	.017
7600	.037	.031	.027	.023
10000	.042	.036	.032	.027
11400	.045	.038	.034	.030
15200	.05	.044	.04	.035

II. Pre-exponential factor assumed to be the average of the values from Table 2.

	900	1000	1100	1200
1000	.0077	.0068	.0062	.0055
1520	.011	.0097	.009	.008
3800	.02	.019	.018	.017
5000	.024	.023	.022	.021
7600	.030	.029	.029	.028
10000	.034	.034	.035	.034
11400	.036	.036	.038	.037
15200	.041	.042	.044	.043

Table 4. Variation of Reduced Rate Constant With Pressure for  $CH_3O$ .

Pressure (torr)	( $k_{uni}/k_{\infty}$ )
1520	.0095
3800	.0185
5000	.0225
7600	.029
10000	.034
11400	.038
15200	.0425

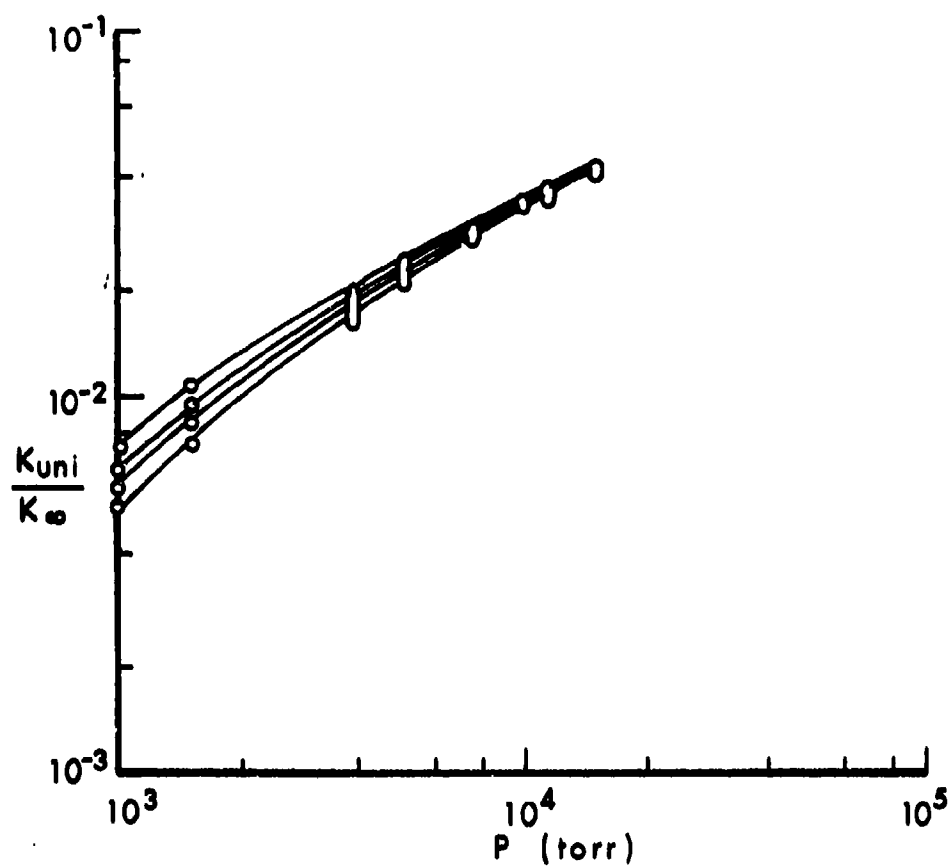


Figure 4. Variation of the reduced rate coefficient,  $k_{uni}/k_{\infty}$ , with pressure for four temperatures, 900°K, 1000°K, 1100°K, and 1200°K.

Table 5. Comparison of RRKM Predictions for  $k_{uni}$  with Predictions of Reduced Fall-off Equation.

	Temperature							
	1200		1100		1000		900	
Pressure	RRKM	Formula	RRKM	Formula	RRKM	Formula	RRKM	Formula
1520	1.1E9	1.3E9	4.9E8	5.3E8	1.8E8	1.8E8	5.1E7	4.7E7
3800	2.4E9	2.4E9	1.0E9	1.1E9	3.5E8	3.3E8	9.6E7	8.5E7
7600	3.9E9	3.8E9	1.6E9	1.5E9	5.4E8	5.1E8	1.4E8	1.3E8
11400	5.1E9	5.0E9	2.1E9	2.0E9	6.7E8	6.6E8	1.7E8	1.7E8
15200	6E9	6E9	2.4E9	2.4E9	7.7E8	7.9E8	1.9E8	2.1E8

the methoxy radical within the pressure and temperature ranges specified by the pyrolysis experiment. In addition, the simple form of the derived expression recommends its use in kinetic models.

#### IV. A PREDICTED RATE CONSTANT FOR FORMYL RADICAL DECOMPOSITION

Before discussing the prediction of  $k_{uni}$  for the reaction,



it should be noted that the formyl radical may not satisfy the criterion for applying RRKM theory. The breaking of a carbon-hydrogen bond in molecules with atoms other than just carbon and hydrogen, is often found to be slower than anticipated. This slow-down in the specific rate of reaction is rationalized as an effect of inefficient intramolecular transfer of vibrational energy, a manifestation of the high frequency for the C-H stretching motion<sup>11</sup>. Since no dynamic study has yet demonstrated that the molecule is a non-RRKM molecule, the RRKM method will be applied to analyze the decomposition reaction.

11. W.C. Hase, private communication.

In contradistinction to the methoxy radical, there is excellent experimental data characterizing the formyl radical. Both a molecular structure and a complete vibrational spectrum are known for the formyl radical ground electronic state. Furthermore, a theoretical investigation of the electronic structure of this radical includes a self-consistent field estimate of the potential-energy hypersurface for the decomposition reaction. This surface provides a molecular structure for the activated complex, as well as an estimate for the critical energy<sup>12</sup>. Given the structure of the complex, it is an easy matter to estimate reasonable values for the vibrational frequencies of the complex. The data used in this study are presented in Table 5.

A thorough theoretical study of the formyl radical potential energy hypersurface predicts a critical energy lower than that predicted by Bruna, et al. The data from the more recent theoretical work will be used in studies of the formyl radical decomposition reaction\*.

The RRKM calculations were performed with the same techniques used for the methoxy decomposition. Five different integrations were made, corresponding to five choices of temperature: 900°, 975°, 1050°, 1125°, and 1200°K. Statistical mechanical parameters for the calculations are given in Table 6, while the predicted rate constants for various temperatures and pressures are given in Table 7. These data are displayed in Figure 5. The reaction is controlled by bimolecular collision processes for all realistic values of pressure for the temperature range considered. An expression for the specific rate for the bimolecular process was given in equation (6),

$$v_{\text{bim}} = k_1(A)(M) \quad (6)$$

To determine an expression for  $k_1$ , the RRKM results for HCO were extended to a pressure of 1 torr, giving an approximate variation of  $k_1$  with temperature. These data are given in Table 8. Using the value of  $k_1$  for  $T=1050^\circ$ , a pre-exponential factor can be derived which can be expected to give good predictions for the other values of  $k_1$ . If it is assumed that the energy in the exponent is just the critical energy, the Arrhenius expression has the form

12. P.J. Bruna, S. Peyerimhoff, and R.J. Buenker, "Ab initio Study of the Structure, Isomers and Vertical Electronic Spectrum of the Formyl Radical HCO", J. Mol. Structure, 32, 217 (1976).

\* See G.F. Adams, G.D. Purvis and R.J. Bartlett, "Double-Excitation Many-Body Perturbation Theory Calculations of Potential Energy Surfaces. I. Formyl Radical", AR-BRL Technical Report, in press.

Table 6. Molecular Data for Formyl Radical and Excited Complex<sup>a</sup>.

Property	Radical	Complex
R <sub>CH</sub>	1.079	1.697
R <sub>CO</sub>	1.19	1.13
∠OCH	130.00	130.00
E <sub>0</sub>	18.0 kcal mol <sup>-1</sup>	
I <sub>XX</sub>	11.75	12.65
I <sub>YY</sub>	10.86	10.58
I <sub>ZZ</sub>	0.89	2.06
ν <sub>1</sub>	2700.00	
ν <sub>2</sub>	1820.00	2150.00
ν <sub>3</sub>	1080.00	100.00

<sup>a</sup>Bond distances are given in angstroms, moments of inertia are given in amu-A<sup>2</sup>, and vibrational frequencies are given in wave numbers.

Table 7. Statistical Mechanical Parameters for Formyl Radical.

Temperature	900	975	1050	1175	1200
Q <sub>1</sub>	4270	4814	5380	5966	6573
Q <sub>1</sub> <sup>‡</sup>	6646	7494	8375	9288	10232
Q <sub>2</sub>	1.3	1.37	1.45	1.53	1.62
log A <sub>∞</sub>	14.82	14.84	14.87	14.89	14.90

$$k_1 = A_0 \exp(-E_0/RT)$$

$$= 5.5E8 \exp(-18000/1.987T) \quad (15)$$

Values of  $k_1$  predicted by this expression for each of the temperatures considered are given in Table 9. The agreement with the extrapolated low-pressure rate constants is good. Given the expression (15) for  $k_1$ , the unimolecular rate constant is

$$k_{\text{uni}} = k_1(P). \quad (16)$$

This expression accurately reproduces the RRKM predictions of the unimolecular rate constant.

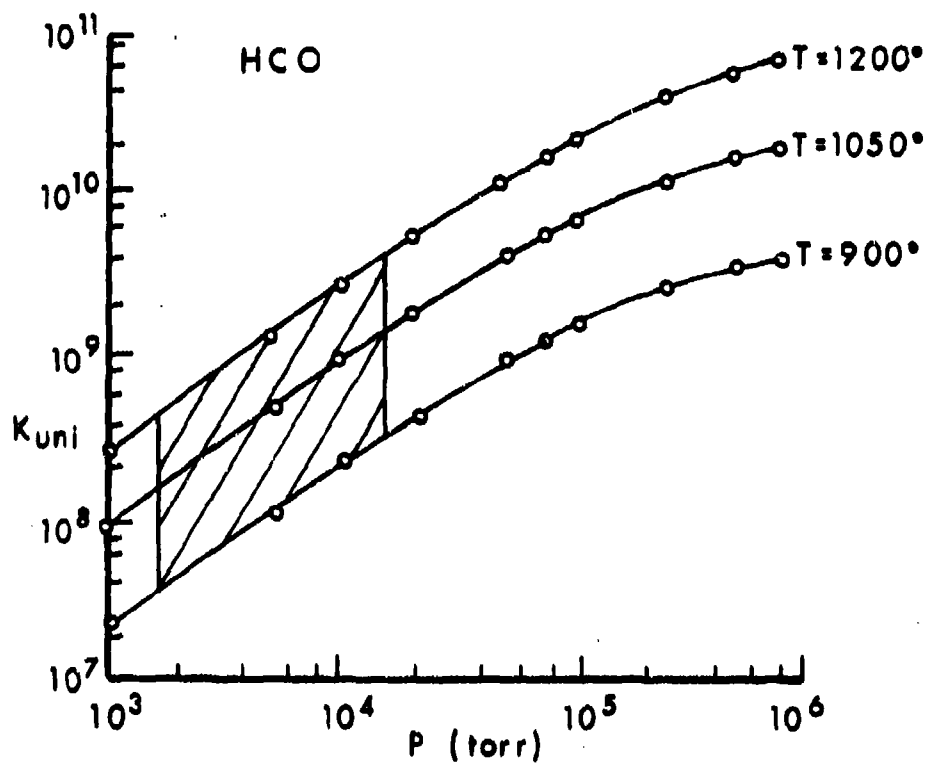


Figure 5. Variation of  $k_{\text{uni}}$  with pressure for the decomposition of formyl radical at three temperatures, 900°K, 1050°K, and 1200°K. The hatched area identifies the physical conditions encountered in Fifer's experiments (1).



Table 8. Predicted  $k_{uni}$  for Formyl Radical.<sup>a</sup>

Pressure (torr)/Temperature (°K)	900	975	1050	1125	1200
1000	2.4(7)	5.2(7)	9.9(7)	1.7(8)	2.8(8)
5000	1.2(8)	2.5(8)	4.9(8)	8.5(8)	1.4(9)
10000	2.3(8)	4.9(8)	9.5(8)	1.7(9)	2.7(9)
20000	4.4(8)	9.5(8)	1.8(9)	3.2(9)	5.3(9)
50000	9.6(8)	2.1(9)	4.1(9)	7.3(9)	1.2(10)
75000	1.3(9)	2.9(9)	5.7(9)	1.0(10)	1.7(10)
100000	1.6(9)	3.6(9)	7.0(9)	1.3(10)	2.1(10)
150000	2.1(9)	4.7(9)	9.3(9)	1.7(10)	2.8(10)
250000	2.7(9)	6.2(9)	1.3(10)	2.3(10)	3.9(10)
500000	3.6(9)	8.4(9)	1.7(10)	3.2(10)	5.6(10)
750000	4.1(9)	9.6(9)	2.0(10)	3.7(10)	6.5(10)
$10^6$	4.4(9)	1.0(10)	2.2(10)	4.1(10)	7.2(10)
$1.5 \times 10^6$	4.7(9)	1.1(10)	2.4(10)	4.5(10)	7.9(10)
$4 \times 10^6$	5.2(9)	1.3(10)	2.7(10)	5.2(10)	9.3(10)
$10^7$	5.5(9)	1.3(10)	2.8(10)	5.5(10)	9.9(10)

<sup>a</sup>Notation: 2.4(7) implies  $2.4 \times 10^7$ .

Table 9. Low Pressure Rate Constants for Formyl Radical.

Temperature	900	975	1050	1125	1200
Extrapolated RRKM	2.4(4)	5.15(4)	9.86(4)	1.72(5)	2.8(5)
Calculated From Equation (15)	2.34(4)	5.08(4)	9.86(4)	1.75(5)	2.9(5)

Fifer reanalyzed the RRKM results replacing pressure with density. For a given density, he estimates an effective activation energy for the bimolecular reaction, and chooses an appropriate pre-exponential factor. His analysis gives log A of 17.0 and activation energy of 20.1 kcal mol<sup>-1</sup>. He then calculates log  $k_{1000} = 12.6$ , which is greater than a value that can be obtained from published data on the reverse reaction<sup>13</sup>, log  $k_{1000} = 11.1$ .

13. D.L. Baulch, D.D. Drysdale, J. Duxbury and S.J. Grant, "Evaluated Kinetic Data for High Temperature Reactions, Vol. 3", Butterworths, London (1976).

Most of the difference between the two estimates can be removed by considering the present treatment of collisional activation. Two variables that affect the collisional activation are the collision diameter,  $\sigma$ , and the collisional efficiency,  $\lambda$ . The collision diameter,  $\sigma$ , was assumed to be 10 angstroms for both the methoxy and formyl decompositions. This value is probably too high for the methoxy study, and it is certainly too high for the formyl radical investigation. Decreasing  $\sigma$  to five angstroms would reduce the predicted rate constants by a factor of 4.

Failure of the strong-collision assumption damages these efforts to predict the rate constant for the decomposition of formyl radical. Simply stated, strong collisions are those which excite a molecule from a reactant state,  $A_1$ , to a state of the energized species,  $A_1^*$ , from which reaction may occur. In present terms the strong collision assumption is  $\lambda=1$ . The necessity to abandon the strong collision hypothesis has been realized only since the 1960's, and theoreticians have concerned themselves with studies of weak collision effects. These efforts have led to recent research by Troe<sup>14,15</sup> and Stace and Murrell<sup>16</sup>.

Stace and Murrell developed an ingenious model to study the effects of pressure and bath gas on the collisional excitation efficiency for small molecules capable of unimolecular decomposition. The results of their research will be discussed in the next report of this series. Here the consequences of Troe's efforts are considered.

Troe calculates the rate constants for thermal unimolecular reactions in the low pressure limit via the solution of the master equation. These rate constants,  $k_0$ , are expressed in terms of a strong collision rate constant,  $k_0^{sc}$ , and a weak collision efficiency,  $\beta_c$ :

$$k_0 = \beta_c k_0^{sc}. \quad (17)$$

Troe transforms this expression into a series of complex equations. The collisional efficiency is the product of a total cross-sectional factor,  $\beta_e$ , such that,

14. J. Troe, "Theory of Unimolecular Reactions at Low Pressures. I. Solutions of the Master Equation.", J. Chem. Phys., 66, 4745 (1977).
15. J. Troe, "Theory of Unimolecular Reactions at Low Pressures. II. Strong Collision Rate Constants. Applications", J. Chem. Phys.
16. A.J. Stace and J.N. Murrell, "Molecular Dynamics and Chemical Reactivity. A Computer Study of Iodine Atom Recombination Under High Pressure Conditions", Molecular Physics, 33, 1, (1977).

$$\beta_c = \beta_\sigma \beta_E . \quad (18)$$

The cross-sectional factor is given by a ratio of an energy dependent collision number and a hard-sphere collision factor, while the step-wise factor is taken to be

$$\beta_c = - < \Delta E > / kTF(E) , \quad (19)$$

where  $< \Delta E >$  is the average internal energy transferred per collision, and  $F(E)$  is a term that corrects for the energy dependence of the density of states. In addition to these relatively simple expressions for the collision-factors, Troe developed a strong-collision rate constant expression that includes factors to correct for changes in the density of states as a function of temperature. Troe's important result, however, is his demonstration that the overall collision efficiency,  $\beta_c$  is a strong function of temperature. He finds that at temperatures near 300°K, collisional efficiencies have values in the range 0.3-0.5, a result which agrees with the available experimental data. At 1000°K, the collisional efficiency has been reduced to a value near 0.1, and corresponding decreases occur at higher temperatures.

Troe's work demonstrates that high temperature studies of low pressure dissociation rate constants correspond to the weak collision limit of energy transfer, where the "strong collision assumption" of unimolecular rate theory has to be abandoned. The experimental conditions of formyl radical decomposition that interest us are high temperature, modest pressure. Consequently, it is expected that the strong collision assumption is not valid for the experimental conditions, nor is the collisional efficiency as low as Troe's estimates suggest. A reasonable guess would assign a value to  $\beta_c$  of 0.2-0.3.

The combination of reduced collision diameter and reduced collisional efficiency will reduce the predicted formyl rate constants by approximately an order-of-magnitude. It is not fruitful to attempt a better estimate of the effect since Troe studied only temperature effects. A more complete treatment of the formyl radical decomposition will be presented in the next report in this series, wherein both temperature and pressure effects will be re-evaluated.

## V. SUMMARY

This is a first effort to predict the rate constants for unimolecular decomposition reactions of small molecular species. The encouraging results suggest that the techniques applied are useful for medium-sized molecules, such as the methoxy radical. However, it seems

clear that simple, direct application of the RRKM method to small, three- and four-atom systems will give results that are of order-of-magnitude accuracy at best. The next report in this series will present two additional analyses of the formyl radical decomposition, with the hope that more accurate results will be obtained.

The calculations reported assumed that the diluent gas was a strong collider. Before applying the data in this report, a modeler should ascertain that the strong-collision assumption applies to the experimental process studied. For those cases where the strong-collision assumption fails, linear scaling of the data contained here should provide a reasonable estimate for the rate constant.

The greatest uncertainty in these calculations is the critical energy,  $E_0$ . Recent developments in electronic structure theory suggest that many-body perturbation theory provides an efficient method for computing the electronic part of the critical energy. Calculations for the formyl radical predict a critical energy of  $18.3 \text{ kcal mol}^{-1}$ , which agrees well with the value assumed in this research<sup>17</sup>. A forthcoming report will discuss these calculations in detail<sup>18</sup>.

17. G.F. Adams, G.D. Bent, G.D. Purvis and R.J. Bartlett, manuscript in preparation.

18. G.F. Adams, G.D. Bent, G.D. Purvis and R.J. Bartlett, ARRADCOM-TR in preparation.

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